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*Research Article*

# Green Chemistry: New Synthesis of Substituted Chromenes and Benzochromenes *via* Three-Component Reaction Utilizing Rochelle Salt as Novel Green Catalyst

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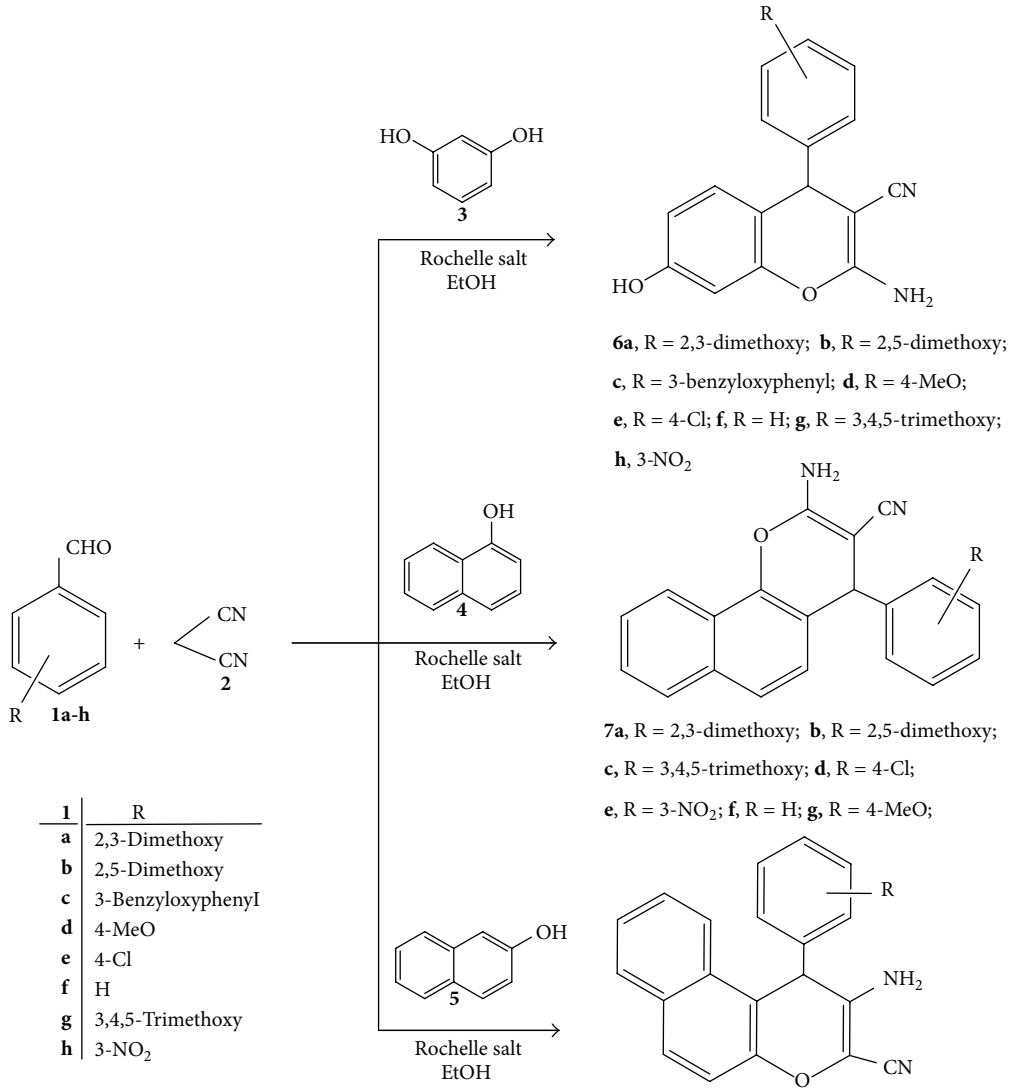
Substituted 2-amino-4-aryl-7-hydroxy-4*H*-chromene-3-carbonitriles (**6**), 2-amino-4-aryl-4*H*-benzo[*h*]chromene-3-carbonitriles (**7**), and 3-amino-1-aryl-1*H*-benzo[*f*]chromenes-2-carbonitriles (**8**) were prepared, in good yields, *via* one-pot three-component reactions of aromatic aldehydes (**1**), malononitrile (**2**), and resorcinol (**3**) or $\alpha$-naphthol (**4**) or $\beta$-naphthol (**5**) in refluxing ethanol or water in the presence of Rochelle salt as novel green heterogeneous and reusable catalyst.

## 1. Introduction

Aminochromenes represent an important class of organic compounds being the main components of many naturally occurring products. In addition, they are valuable precursors used for the synthesis of cosmetics, pigments [1], and potentially biodegradable agrochemicals [2]. Furthermore, fused chromenes are important constituents of pharmacologically active compounds, as these systems have displayed a broad spectrum of biological activities such as antimicrobial [3, 4], mutagenicity [5], antiviral [6], antiproliferative [7], sex pheromonal [8], antitumor [9], central nervous system (CNS) activities [10], and inhibitors of influenza virus sialidases [11, 12]. One-pot multicomponent reactions have received considerable attention in synthetic chemistry as they can produce target products from readily available starting materials in one reaction step without isolating the intermediates thus reducing reaction times, labor cost, and waste production [13]. In addition, water has emerged as a versatile solvent for organic reactions in the last two decades since it is readily available, inexpensive, environmentally benign, neutral, and a natural solvent [14, 15]. For these reasons, water has been used for MCRs as well [16, 17]. MCRs in water are of outstanding value in organic synthesis and green chemistry [16, 17]. Aminochromenes have been prepared by heating a mixture of malononitrile, aldehyde, and activated phenol or naphthols in refluxing DMF or acetonitrile in the presence of hazardous organic bases such as piperidine and triethylamine [18, 19]. Although different synthetic methods to prepare these heterocyclic systems have been reviewed [20–36], to the best of our knowledge, the use of clean solvents in combination with heterogeneous and reusable catalysts to synthesize these systems has not been largely reported [13, 25]. In continuation of our work concerning the synthesis and biological evaluation of new heterocycles [37–40] and aiming to explore the efficiency of Rochelle salt (R. S.) as a novel green heterogeneous and reusable catalyst in the one-pot reactions in the organic syntheses, we report herein our results on the utility of Rochelle salt (R. S.) as a green catalyst in the three-component condensations between aromatic aldehydes, active methylene reagents, and activated phenols.

## 2. Result and Discussion

Our synthesis began with the reaction of a mixture of aromatic aldehydes **1a–h**, malononitrile (**2**), and resorcinol (**3**) in refluxing ethanol containing a catalytic amount of Rochelle salt to give 2-amino-4-aryl-7-hydroxy-4*H*-chromene-3-carbonitriles **6a–h** (Scheme 1), (Table 1).




| 1 | R |
|---|---|
| a | 2,3-Dimethoxy |
| b | 2,5-Dimethoxy |
| c | 3-BenzyloxyphenyI |
| d | 4-MeO |
| e | 4-Cl |
| f | H |
| g | 3,4,5-Trimethoxy |
| h | 3-$NO_2$ |

Scheme 1: Synthesis of compounds **6–8**.

The structures of the isolated products **6a-h** were confirmed on the basis of their elemental analyses and spectral data. The IR spectrum of the reaction products showed the presence of both OH and $NH_2$ functions at 3496–3320 $cm^{-1}$ and a cyano at ~2200 $cm^{-1}$. The $^1H$ NMR spectra displayed the presence of two singlets at $\delta$ = 6.37–6.87 and 9.39–9.61 ppm attributable to the amino ($NH_2$) and OH groups, respectively. Furthermore, the $^1H$ NMR gave strong evidence for the formation of compounds **6a–h**. The data confirmed the presence of the H-4 proton at $\delta$ = 4.57–4.92 ppm, in addition to the signals of aromatic protons and other groups (see Table 3). Moreover, their structures were supported by both correct mass spectra and analytical data, which were compatible with the proposed structures for compounds **6a-h**.

Since our interest is in developing a synthetic approach with a view to synthesize new derivatives of the interesting aminochromenes, $\alpha$-naphthol (**4**) and $\beta$-naphthol (**5**), good precursors for this purpose, were thus investigated. Reacting a mixture of aromatic aldehydes **1a–h**, malononitrile (**2**) and $\alpha$-naphthol (**4**) or $\beta$-naphthol (**5**), under the same reaction conditions, gave the 2-amino-4-aryl-4*H*-benzo[*h*]chromene-3-carbonitriles **7a-g** and 3-amino-1-aryl-1*H*-benzo[*f*]-chromenes-2-carbonitriles **8a-h**, respectively, in good yields. The structures of these products (**7**) and (**8**) were established by correct elemental analyses and spectral data, which were compatible with the assigned structures. (*cf.* Tables 2 and 3).

On the other hand, heating a mixture of aromatic aldehydes (**1a–h**), malononitrile (**2**), and resorcinol (**3**) in boiling water containing a catalytic amount of Rochelle salt gave 2-amino-4-aryl-7-hydroxy-4*H*-chromene-3-carbonitriles **6a–h**, in excellent yields. In contrast, neither $\alpha$-naphthol nor

Table 1: Yields and melting points of the synthesized compounds **6–8**.

| Compound | R | Yield % | Observed m.p. | Reported m.p. | References |
|---|---|---|---|---|---|
| **6a** | 2,3-Dimethoxy | 85 | 250 | — | — |
| **6b** | 2,5-Dimethoxy | 85 | 170 | — | — |
| **6c** | 3-Benzyloxyphenyl | 86 | 230 | — | — |
| **6d** | 4-MeO | 86 | 112–114 | 111-112 | [30, 32] |
| **6e** | 4-Cl | 90 | 184 | 164 | [30] |
| **6f** | H | 80 | 228 | 231 | [32] |
| **6g** | 3,4,5-Trimethoxy | 85 | 210 | 205 | [34] |
| **6h** | 3-$NO_2$ | 84 | 170 | 169-170 | [32] |
| **7a** | 2,3-Dimethoxy | 85 | 260 | — | — |
| **7b** | 2,5-Dimethoxy | 75 | 240 | — | — |
| **7c** | 3,4,5-Trimethoxy | 80 | 190 | 189 | [35] |
| **7d** | 4-Cl | 90 | 235 | 232 | [20] |
| **7e** | 3-$NO_2$ | 82 | 210 | 212 | [20] |
| **7f** | H | 90 | 205 | 205 | [20] |
| **7g** | 4-MeO | 84 | 204 | 205 | [35] |
| **8a** | 2,3-Dimethoxy | 80 | 240 | — | — |
| **8b** | 2,4-Dimethoxy | 80 | 205 | — | — |
| **8c** | 2,5-Dimethoxy | 75 | 206 | — | — |
| **8d** | 3,4,5-Trimethoxy | 85 | 209 | — | — |
| **8e** | 3-$NO_2$ | 81 | 195 | 190 | [29] |
| **8f** | 4-MeO | 92 | 260 | 255 | [26] |
| **8g** | H | 90 | 280 | 278–280 | [20] |
| **8h** | 4-Cl | 83 | 187 | 191 | [29] |

Table 2: Elemental analyses of the newly synthesized compounds **6–8**.

| Compound | Mol. formula/M.Wt. | | Elemental analysis | | |
|---|---|---|---|---|---|
| | | | C% | H% | N% |
| **6a** | $C_{18}H_{16}N_2O_4$ (324.35) | Calc. | 66.66 | 4.97 | 8.64 |
| | | Found | 66.41 | 5.12 | 8.34 |
| **6b** | $C_{18}H_{16}N_2O_4$ (324.35) | Calc. | 66.66 | 4.97 | 8.64 |
| | | Found | 67.01 | 5.13 | 9.01 |
| **6c** | $C_{23}H_{18}N_2O_3$ (370.40) | Calc. | 74.58 | 4.90 | 7.56 |
| | | Found | 76.86 | 4.75 | 7.15 |
| **7a** | $C_{22}H_{18}N_2O_3$ (358.39) | Calc. | 73.73 | 5.06 | 7.82 |
| | | Found | 74.11 | 5.20 | 8.07 |
| **7b** | $C_{22}H_{18}N_2O_3$ (358.39) | Calc. | 73.73 | 5.06 | 7.82 |
| | | Found | 74.02 | 5.38 | 7.58 |
| **8a** | $C_{22}H_{18}N_2O_3$ (358.39) | Calc. | 73.73 | 5.06 | 7.82 |
| | | Found | 74.11 | 5.74 | 8.21 |
| **8b** | $C_{22}H_{18}N_2O_3$ (358.39) | Calc. | 73.73 | 5.06 | 7.82 |
| | | Found | 73.63 | 4.83 | 8.19 |
| **8c** | $C_{22}H_{18}N_2O_3$ (358.39) | Calc. | 73.73 | 5.06 | 7.82 |
| | | Found | 73.52 | 5.24 | 7.63 |
| **8d** | $C_{23}H_{20}N_2O_4$ (388.42) | Calc. | 71.12 | 5.19 | 7.21 |
| | | Found | 71.34 | 5.40 | 7.50 |

$\beta$-naphthol underwent the above one-pot three-component reactions in boiling water even upon heating for extended periods. When, a mixture of ethanol/water was used as a solvent in the previous reactions, the three phenols gave the desired products **6a–h**, **7a–g,** and **8a–h**, in good yields. All known compounds were identical in all physical and spectroscopic aspects with the others which are reported in literatures.

Table 3: Spectral data of the newly synthesized compounds **6–8**.

| Compound | IR ($cm^{-1}$) | MS | $^1H$ NMR (DMSO-$d_6$) ($\delta$ ppm) |
|---|---|---|---|
| **6a** | 3419–3327 (OH and $NH_2$), 2190 (CN) | 324 ($M^+$) | 3.65 (s, 3H, $OCH_3$), 3.70 (s, 3H, $OCH_3$), 4.89 (s, 1H, H-4), 6.75 (s, 2H, $NH_2$), 6.45–6.74 (m, 6H, ArH), 9.61 (br s, 1H, OH). |
| **6b** | 3430–3325 (OH and $NH_2$), 2210 (CN) | 324 ($M^+$) | 3.68 (s, 3H, $OCH_3$), 3.73 (s, 3H, $OCH_3$), 4.92 (s, 1H, H-4), 6.37 (s, 2H, $NH_2$), 6.53–6.75 (m, 6H, ArH), 9.51 (br s, 1H, OH). |
| **6c** | 3430–3320 (OH and $NH_2$), 2215 (CN) | 370 ($M^+$) | 4.57 (s, 1H, H-4), 5.04 (s, 2H, $-CH_2-$), 6.75–6.82 (m, 5H, ArH), 6.87 (s, 2H, $NH_2$), 7.22–7.37 (m, 3H, ArH), 7.40–7.44 (m, 4H, ArH), 9.39 (br s, 1H, OH), |
| **7a** | 3387, 3310 ($NH_2$), 2190 (CN) | 358 ($M^+$) | 3.64 (s, 3H, $OCH_3$), 3.79 (s, 3H, $OCH_3$), 5.14 (s, 1H, H-4), 6.69 (s, 2H, $NH_2$), 7.0–7.53 (m, 9H, ArH). |
| **7b** | 3387, 3315 ($NH_2$), 2195 (CN) | 358 ($M^+$) | 3.71 (s, 3H, $OCH_3$), 3.80 (s, 3H, $OCH_3$), 4.54 (s, 1H, H-4), 6.72 (s, 2H, $NH_2$), 7.10–7.53 (m, 9H, ArH). |
| **8a** | 3460, 3340 ($NH_2$), 2200 (CN) | 358 ($M^+$) | 3.85 (s, 3H, $OCH_3$), 4.01 (s, 3H, $OCH_3$), 4.62 (s, 1H, H-4), 6.66 (s, 2H, $NH_2$), 7.21–7.45 (m, 9H, ArH). |
| **8b** | 3445, 3300 ($NH_2$), 2201 (CN) | 358 ($M^+$) | 3.82 (s, 3H, $OCH_3$), 3.90 (s, 3H, $OCH_3$), 4.54 (s, 1H, H-4), 6.72 (s, 2H, $NH_2$), 7.28–7.53 (m, 9H, ArH). |
| **8c** | 3450, 3320 ($NH_2$), 2187 (CN) | 358 ($M^+$) | 3.73 (s, 3H, $OCH_3$), 3.82 (s, 3H, $OCH_3$), 4.55 (s, 1H, H-4), 6.69 (s, 2H, $NH_2$), 7.29–7.52 (m, 9H, ArH). |
| **8d** | 3465, 3310 ($NH_2$), 2191 (CN) | 388 ($M^+$) | 3.70 (s, 3H, $OCH_3$), 3.81 (s, 3H, $OCH_3$), 3.89 (s, 3H, $OCH_3$), 4.50 (s, 1H, H-4), 6.64 (s, 2H, $NH_2$), 7.11–7.78 (m, 8H, ArH). |

## 3. Conclusions

We have discovered a green and efficient synthetic route to some new chromenes, namely, 2-amino chromenes, benzo[*h*]chromenes and benzo[*f*]chromenes, of expected biological interest, by utilizing Rochelle salt as novel green catalyst. To the best of our knowledge, this is the first time for utilizing Rochelle salt, as an efficient, green, and cheap catalyst in the one-pot three-component reactions.

## 4. Experimental

*4.1. General.* All melting points were measured on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded with a Shimadzu FT-IR 8101 PC spectrophotometer in KBr disks. $^1H$ NMR spectra were recorded with Bruker AM 300 spectrometer at 300 MHz with DMSO-$d_6$ and $CDCl_3$ as solvents and TMS as an internal standards; chemical shifts ($\delta$) are reported in ppm. Mass spectra were measured on a GCMS-QP1000 EX (EI, 70 eV) mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 plates, 0.25 mm thick with F-254 indicator. Visualization was accomplished by UV light. Solvents for chromatography were reagent grad and used as received. Microanalyses were performed by the microanalytical Data Unit at Cairo University.

*General Procedure for the Synthesis of 2-Amino-4-aryl-7-hydroxy-4H-chromene-3-carbonitriles 6a–h.*

*Method (A)*. To a mixture of equimolar amounts of aromatic aldehydes **1a–h**, malonontirile (**2**), and resorcinol (**3**) (5 mmol) in ethanol or ethanol/water mixture (1 : 1) (10 mL), Rochelle salt (0.30 g) was added. Then, the reaction mixture was heated at reflux temperature for 2–4 h. After cooling to room temperature, the resulting solid products were collected by filtration, dried, and recrystallized from EtOH to give chromenes **6a–h**.

*Method (B)*. To a mixture of equimolar amounts of aromatic aldehydes **1a–h**, malononirile (**2**), and resorcinol (**3**) (5 mmol) in $H_2O$ (10 mL), Rochelle salt (0.3 g) was added. Then, the reaction mixture was worked up as described above to give chromenes **6a–h**.

*General Procedure for the Synthesis of 2-Amino-4-aryl-4H-benzo[h]chromene-3-carbonitriles 7a–g and 3-Amino-1-aryl-1H-benzo[f]chromenes-2-carbonitriles 8a–h.* To a mixture of equimolar amounts of aromatic aldehydes **1a–h**, malononirile (**2**) and 1-naphthol (**4**) (or 2-naphthol (**5**)) (5 mmol) in ethanol or ethanol/water mixture (1 : 1) (10 mL), Rochelle salt (0.3 g) was added. The reaction mixture was refluxed for 4–8 h. After cooling to room temperature, the resulting solid products were collected by filtration, dried, and recrystallized from EtOH to give the products **7a–g** and **8a–h**, respectively.

## Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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